

# Modification of the ground state in Sm-Sr manganites by oxygen isotope substitution

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The effect of  $^{16}\text{O} \rightarrow ^{18}\text{O}$  isotope substitution on electrical resistivity and magnetic susceptibility of  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  manganites is analyzed. It is shown that the oxygen isotope substitution drastically affects the phase diagram at the crossover region between the ferromagnetic metal state and that of antiferromagnetic insulator ( $0.4 < x < 0.6$ ), and induces the metal-insulator transition at for  $x = 0.475$  and  $0.5$ . The nature of antiferromagnetic insulator phase is discussed.

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Despite intense studies, the nature of the colossal magnetoresistance in manganites is still a matter of hot debate. This phenomenon is usually observed when the system is close to a borderline between ferromagnetic metallic (FM) phase and an insulating (I) one. The type of the latter may be different (paramagnetic or antiferromagnetic (AF)), but there are more and more indications that there exists also some kind of charge ordering (CO) – either real long-range CO (see review article [1] and references therein) or, at least, short-range CO correlations [2, 3]. When the system is close to a FM-I crossover, even weak perturbations can induce this crossover: change of temperature [4], magnetic field [5], pressure [6], irradiation [7], *etc.* In La-Nd-Ca [8] and La-Pr-Ca [9] manganites, one can induce this crossover and consequently the metal-insulator transition even by changing the oxygen isotope content: whereas the low-temperature state of  $^{16}\text{O}$  samples is FM, the samples  $^{18}\text{O}$  become CO AF insulator. This was confirmed by direct neutron scattering study [10].

The question arises whether this spectacular phenomenon is confined only to this particular situation of insulating phase with the charge ordering and the CE-type magnetic structure, i.e. whether the nature of competing phases, in particular, the insulating one, is crucial, or one can get similar behavior in other systems close to the FM-I crossover. In studying this question, we have found yet another system with the metal-insulator transition induced by the oxygen isotope substitution:  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  with  $x$  in the  $0.475$ – $0.5$  range. The neutron scattering results for this system at  $x=0.4$  [11] and preliminary data for  $x=0.45$  with  $^{18}\text{O}$  [12] suggest that, in contrast to (La,Pr)CaMnO<sub>3</sub>, the insulating phase here

has not the CE, but most probably A-type antiferromagnetic structure. If so, we could conclude that the metal-insulator transition induced by the isotope substitution is a general property of a FM-I crossover independent of the detailed nature of the insulating phase. Let us also note here that X-ray, neutron, and electron diffraction demonstrated possible existence of a short-range charge ordering for  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  in the concentration range under discussion [13]. The results of ESR [14] and Raman [15] measurements lead to the same conclusion.

Ceramic  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  samples were prepared by the solid-state reaction technique, the detailed procedure is described in Ref. 16. The enrichment of the samples by  $^{18}\text{O}$  was performed at  $T = 950^\circ\text{C}$  and at pressure  $p = 1$  bar during 200 hours using the method reported in Refs. 9, 17. The resistivity of the samples was measured by the conventional four-probe technique in the temperature range from  $4.2$  to  $300$  K. The measurements of real part of ac magnetic susceptibility  $\chi'(T)$  were performed in ac magnetic field with frequency  $667$  Hz and amplitude of about  $0.4$  Oe.

The temperature dependence of electrical resistivity  $\rho(T)$  for  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  samples with  $x = 0.425, 0.450, 0.475, 0.500$ , and  $0.525$  annealed both in  $^{16}\text{O}$  and  $^{18}\text{O}$  atmosphere is presented in Fig. 1. Four  $^{16}\text{O}$ -containing samples, with  $x = 0.425, 0.450, 0.475$ , and  $0.500$ , are characterized by a metal-like behavior at low temperatures, Fig. 1a. With the growth of  $x$ , the resistivity increases and the metal-insulator transition point  $T_{MI}$  shifts toward lower temperatures ( $T_{MI}$  was determined as a point corresponding to the maximum temperature derivative of  $\rho(T)$  below the resistivity peak). This can be attributed to the narrowing of the electron bandwidth

and the weakening of ferromagnetic interaction. The sample with  $x = 0.525$  is an insulator down to the lowest temperatures.

After the  $^{16}\text{O} \rightarrow ^{18}\text{O}$  isotope substitution, only two samples with the lowest Sr content ( $x = 0.425$  and  $0.450$ ) remain metal-like at low temperatures, the other become insulating (Fig. 1b). These metallic samples have much higher resistivity than those with  $^{16}\text{O}$ .  $T_{MI}$  decreases by 40 K and 60 K for the samples with  $x = 0.425$  and  $0.450$ , respectively. For  $x = 0.475$  and  $0.500$ , we observed the metal-insulator transition induced by the oxygen isotope substitution (see inset in Fig. 1a) similar to that reported for La-Pr manganites [9]. Thus, in this system, the  $^{16}\text{O} \rightarrow ^{18}\text{O}$  isotope substitution leads to the changes in the phase diagram: the weakening of the ferromagnetism and the stabilization of the insulating (probably CO) phase. A more pronounced thermal hysteresis in  $\rho(T)$  curves for the  $^{18}\text{O}$  samples is a manifestation of their enhanced inhomogeneity. A relatively low magnetic field ( $H = 1$  T) transforms the samples with  $^{18}\text{O}$  to the metal-like state and suppresses the contribution from the high-resistivity insulating state (for  $x=0.500$  see inset in Fig. 1b).

The temperature dependence of the ac magnetic susceptibility  $\chi'(T)$  for  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  system is presented in Fig. 2. The steep growth of  $\chi'(T)$  corresponds to the onset of FM ordering; the Curie temperature  $T_C$  was determined as a point corresponding to the maximum  $d\chi'(T)/dT$ . For samples with  $^{16}\text{O}$  and  $x = 0.425, 0.450$ , and  $0.475$ ,  $\chi'(T)$  behaves in a similar manner (as far as the magnitude of  $\chi'$  and  $T_C$  are concerned). One sees that these samples are essentially ferromagnetic. The behavior of  $\chi'$  at low temperatures (decrease after reaching a maximum) is apparently connected with the effect of magnetic domains, see Ref. 18.

For  $x = 0.500$ , the  $\chi'$  value drops drastically,  $T_C$  shifts toward lower temperatures, this is a signature of the decreasing contribution of FM phase. For the composition with  $x = 0.525$  the susceptibility becomes very small, and the ferromagnetism almost disappears. In the samples with  $^{18}\text{O}$ , for compositions with  $x \geq 0.450$  the  $\chi'$  value is significantly lower in comparison to the samples with  $^{16}\text{O}$ ,  $T_C$  is also much lower and the hysteresis appears. The FM phase content decreases so steeply that it becomes insufficient for the percolation in the samples with  $x = 0.475$  and  $0.500$ , as it is clearly seen for the corresponding  $\rho(T)$  curves. The FM-CO phase boundary shifts toward the CO state.

The temperature dependence of inverse ac magnetic susceptibility  $1/\chi'(T)$  for  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  manganite samples with  $^{16}\text{O}$  and  $^{18}\text{O}$  is shown in insets in Figs. 2a and 2b, respectively. Above the magnetic ordering temperature, the behavior of  $1/\chi'(T)$  curves is rather complicated suggesting the existence of an inhomogeneous state even in the paramagnetic region. At relatively high temperatures,  $T \sim 250\text{--}300$  K, all  $1/\chi'(T)$  are very close to each other exhibiting a nearly linear growth of the

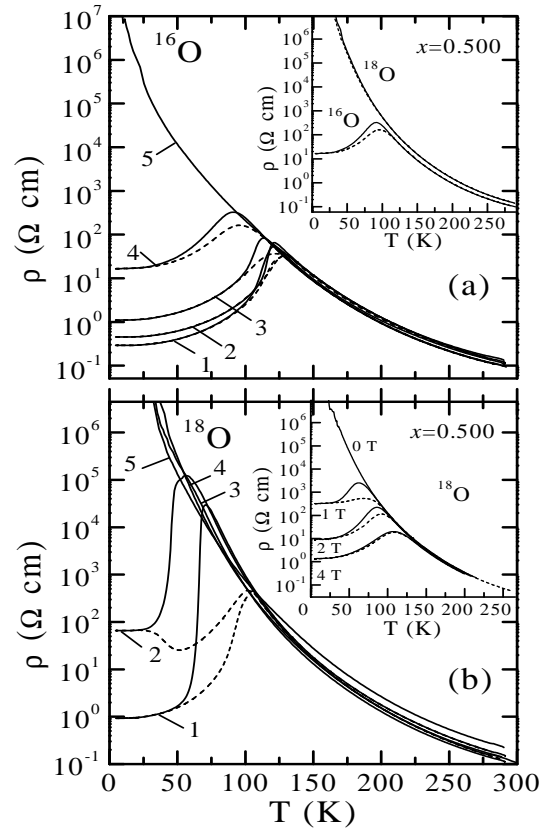


FIG. 1: Temperature dependence of electrical resistivity for  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  with  $x = 0.425$  (1),  $0.450$  (2),  $0.475$  (3),  $0.500$  (4), and  $0.525$  (5). The results for samples with  $^{16}\text{O}$  and  $^{18}\text{O}$  are presented at panels (a) and (b), respectively. The inset in panel (a) illustrates the metal-insulator transition induced by the oxygen isotope substitution for samples with  $x = 0.500$ . The inset in panel (b) shows the evolution of resistivity with increasing magnetic field for the  $^{18}\text{O}$  sample with  $x = 0.500$ . Solid and dashed lines correspond to cooling and heating, respectively.

Curie-Weiss type. With the temperature lowering, the curves flatten, the flattening being more pronounced for larger  $x$ . For  $x = 0.475$ ,  $x = 0.500$ , we can see even a plateau in  $1/\chi'(T)$ . The onset temperature for the flattening and deviation of  $1/\chi'(T)$  curves for different  $x$  from each other seems to be related to the arising CO correlations ( $T_{CO} \approx 240$  K). This value agrees with the data of Refs. 14, 19. The behavior of  $1/\chi'(T)$  at  $T < T_{CO}$  can be interpreted in a picture of interacting and competing FM and CO correlations, the latter growing with  $x$ . Similar behavior was reported in Ref. 4.

At  $T > T_C$ , the  $^{16}\text{O} \rightarrow ^{18}\text{O}$  isotope substitution does not change the general features of  $1/\chi'(T)$  curves: the deviations from the Curie-Weiss law begin at the same temperature, below which the slope of  $1/\chi'(T)$  is virtually independent of the isotope content at a given value of  $x$ . However, for the heavier isotope,  $T_C$  becomes lower and  $1/\chi'$  increases. Thus, for the samples with  $^{18}\text{O}$ , the

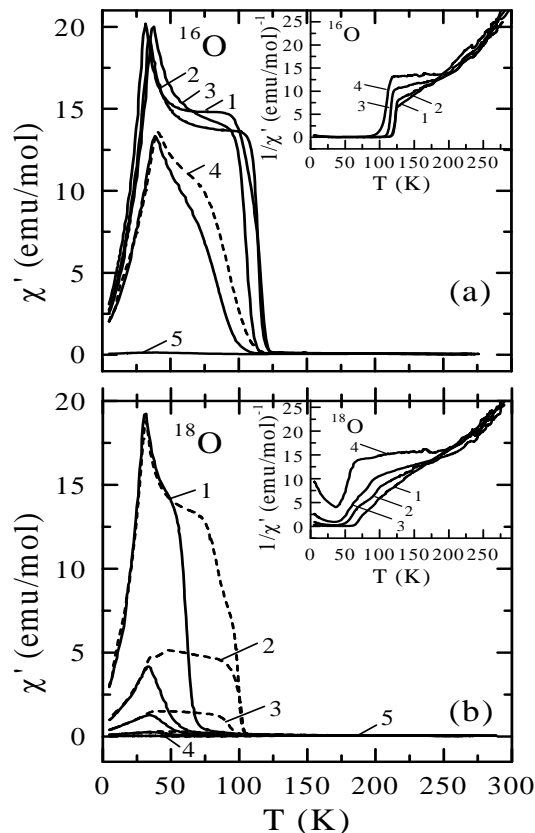


FIG. 2: Temperature dependence of ac magnetic susceptibility for  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  with  $x = 0.425$  (1),  $0.450$  (2),  $0.475$  (3),  $0.500$  (4), and  $0.525$  (5). The behavior of the inverse susceptibility is illustrated in the insets. The results for samples with  $^{16}\text{O}$  and  $^{18}\text{O}$  are presented at panels (a) and (b). Solid and dashed lines correspond to cooling and heating, respectively.

plateau in  $1/\chi'(T)$  curves is observed within a wider temperature range. We can argue that the AFM correlations related to the charge ordering arise in the  $^{18}\text{O}$  samples at the same temperature  $T_{\text{CO}} \approx 240$  K, but exist down to lower temperatures, i.e. the FM interaction becomes weaker and the CO-FM equilibrium shifts toward the CO state. In the samples with  $^{18}\text{O}$ , the transition to the FM state is characterized by a broader hysteresis in comparison to that than for the  $^{16}\text{O}$  samples.

From the data presented above one sees that the  $^{16}\text{O} \rightarrow ^{18}\text{O}$  isotope substitution induces the metal-insulator transition close to the crossover to an insulating state. According to Ref. 13, for  $^{16}\text{O}$  samples such a crossover starts already at  $x = 0.4$  and extends up to  $x = 0.6$ . As follows from our data, the actual change of the ground state occurs at  $x \sim 0.5$  (although an inhomogeneous state with some traces of the FM phase may exist up to  $x = 0.6$ ).

The exact nature of an insulating phase for  $x \geq 0.5$  is not yet established with certainty, but the neutron scattering data [12] show that it is an *A*-type antifer-

romagnet. This agrees with the general trend characteristic of  $\text{R}_{1-x}\text{Sr}_x\text{MnO}_3$  manganites where the *A*-type “bad metal” state was observed for  $x \approx 0.5$  in compounds with  $\text{R} = \text{La}$  [20] and  $\text{R} = \text{Nd}$  [21], and with the theoretical considerations [22, 23]. In our case, this state is insulating but the resistivity and the energy gap in it at low temperatures are much smaller than in  $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  with  $y = 0.75$ , for which the isotope-induced metal-insulator transition was first observed in Ref. 9. Indeed, whereas the room temperature resistivities of these two systems are comparable ( $0.29 \text{ Ohm}\cdot\text{cm}$  in  $(\text{SmSr})\text{MnO}_3$  *vs*  $0.37 \text{ Ohm}\cdot\text{cm}$  in  $(\text{LaPr})\text{CaMnO}_3$ ), the resistivities at  $60 \text{ K}$  are already much different:  $3.5 \cdot 10^3 \text{ Ohm}\cdot\text{cm}$  for  $\text{SmSr}$  system *vs*  $2.9 \cdot 10^7 \text{ Ohm}\cdot\text{cm}$  for  $(\text{LaPr})\text{Ca}$  one. Note that the samples of both systems had similar porosity and mean grain size. The effective activation energies at lowest temperatures can be estimated as  $\sim 15 \text{ meV}$  for the  $\text{SmSr}$  case but  $\sim 120 \text{ meV}$  for  $(\text{LaPr})\text{Ca}$ .

The insulating behavior of  $\text{SmSr}$  samples be either related to the granular nature of our samples as contrasted with the single crystals studied in [24], or may be due to a formation of some weak superstructure of the CO type [13]. As follows from the results of [24], the *A*-type AFM single crystals show metal-like behavior in the *ab*-plane, but are insulating in *c*-direction. This can lead to an insulating behavior with small activation energy in our ceramic samples.

Another factor may be a possible instability of a metallic state. Most probably, the occupied orbitals in the *A*-type  $\text{SmSr}$  insulating phase for  $x \geq 0.5$  are of  $x^2 - y^2$  type [21, 22, 23], whereas these are ordered  $3x^2 - r^2$  and  $3y^2 - r^2$  in  $(\text{LaPr})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , the latter having the conventional charge ordering with the CE magnetic structure. The existence of a small energy gap in the *A*-type  $\text{SmSr}$  system may be related to the instability of a metallic state: the Hubbard subband of  $x^2 - y^2$  type will have spectrum  $\varepsilon(k) = -2t(\cos k_x + \cos k_y)$  and it will be half filled at  $x = 0.5$ , which would give a nested Fermi surface. This can lead to a charge-density-wave state with the opening of a small gap. This should also give a superstructure with the wavevector  $q = (\frac{1}{2}, \frac{1}{2}, 0)$  – the same as in the usual CO state, but with much weaker distortions. It would be interesting to look for such weak superstructure experimentally.

The present results show that the isotope substitution can drastically change the properties of the system when it is close to a FM-I crossover independent of the detailed nature of the I phase. For the  $(\text{LaPr})\text{Ca}$  system, this I state is a “strong” insulator with the charge ordering and the CE magnetic ordering, whereas here, in  $\text{SmSr}$  system, it is a weak insulator of the *A*-type. Nevertheless the effect of the isotope substitution is similar.

The detailed mechanism of the isotope effect on the properties of manganites is not yet completely clear, but most probably it is connected with the decrease in the

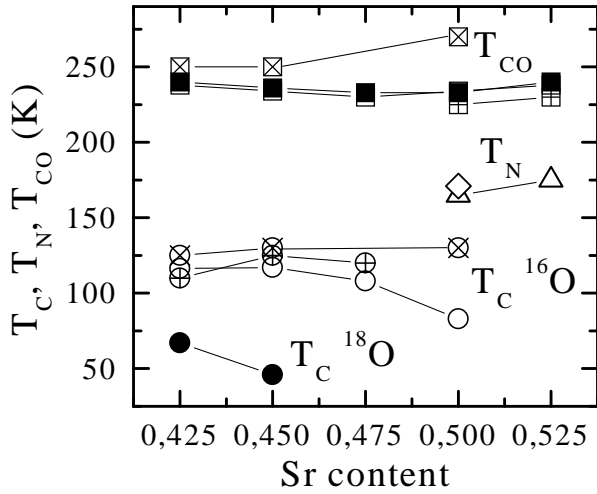


FIG. 3: The Curie, Néel, and charge ordering temperatures for  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  samples under study. Open and solid symbols correspond to the samples with  $^{16}\text{O}$  and  $^{18}\text{O}$ , respectively.  $\otimes$ ,  $\diamond$ ,  $\boxtimes$  and  $\oplus$ ,  $\triangle$ ,  $\boxplus$  are the data from [14] and [19] for  $T_C$ ,  $T_N$ ,  $T_{CO}$ .

electron bandwidth for heavier isotopes either due to zero-point oscillations or to polaronic effects [17, 25]. This is consistent with the change of  $T_{CO}$  and  $T_C$  with the isotope content shown in Fig. 3. The CO state is relatively insensitive to the isotope composition, which is quite natural if the mechanism of CO (or CDW) is predominantly electron-lattice interaction [26] (as is well known, the dimensionless electron-phonon coupling constant  $\lambda$  does not depend on the mass of ions). On the contrary,  $T_C$  in the double exchange model scales with the bandwidth, and the decrease in  $T_C$  with the growth of oxygen mass (Fig. 3) is consistent with this interpretation.

Summarizing, we studied the effect of the oxygen isotope substitution on the properties of  $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$  in the most interesting concentration range  $0.4 \leq x \leq 0.6$ . It was shown that close to a crossover from the ferromagnetic metallic state ( $x \leq 0.5$ ) to an antiferromagnetic insulator ( $x \geq 0.5$ ) all the properties change drastically – up to the fact that for  $x = 0.475$  and  $0.5$  one even induces the metal-insulator transition by the  $^{16}\text{O} \rightarrow ^{18}\text{O}$  substitution. Most probably this substitution transforms the FM state to an A-type antiferromagnet. We speculate that the relevant orbitals in this state are  $x^2 - y^2$  ones and the energy gap appears due to the formation of a charge

density wave in the  $x^2 - y^2$  band. We conclude that this transition is induced by the decrease of the bandwidth for heavier ions. The results obtained, together with the earlier observed isotope-induced metal-insulator transition in  $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , show that the isotope substitution is a powerful tool both for modifying the properties of manganites close to a crossover between different states and for the study of their physical characteristics.

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